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14. ABSTRACT
Amphiphilic block copolymers have been added to two-part epoxy resin and cured leading to well-defined nanocomposites. Reactive and non-reactive polar blocks were coupled to non-polar hydrocarbon blocks using anionic and living free-radical polymerization techniques. Mixtures containing 0 to 100% block copolymer were investigated for structure by small-angle X-ray scattering and transmission electron microscopy, and for mechanical properties by compact tension testing. Spherical micelles and vesicles were documented at low block concentrations, and these nanocomposites exhibit enhanced fracture toughness. Chemical bond formation between the matrix and block copolymer leads to some improvement in toughness.

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Block Copolymer-Based Thermoset Nanocomposites

Introduction

This research program was inspired by the discovery that symmetric poly(ethyleneoxide)-poly(ethylenepropylene) (PEO-PEP) diblock copolymers, added to BPA348/MDA, a two-part epoxy/hardener resin, would remain distributed in the same nanoscale morphology throughout thermal curing. This result is counterintuitive. Long established experiments and theory dealing with network forming condensation polymerization reactions in the presence of linear homopolymers show that macroscopic phase separation accompanies gelation since the weight-average molecular weight (M_W) diverges. Blends of the epoxy resin and diblock copolymer form ordered phases (spheres (S), cylinders (C), gyroid (G), lamellae(L)) at higher concentrations and disordered micelles at lower concentrations with domain dimensions characteristic for segregated block copolymers. All but the gyroid phase remain intact as the epoxy hardens, resulting in clear pieces of glassy plastic. This preliminary finding is now being exploited in various ways, to toughen thermosetting compounds and elucidate the failure mechanisms as a function of morphology, block copolymer concentration, and interfacial bonding, as discussed in the following subsections.

Asymmetric PEP-PEO Diblocks

Interfacial curvature is controlled primarily by the composition of the block copolymer. Pure A-B diblock copolymers produce a well-defined sequence of four morphologies (L, G, C, S) as the volume fraction f_A of the A block increases from 0.5 to 1.0 (or decreases from 0.5 to 0). Adding type A homopolymer to an A-B diblock induces a similar effect provided the homopolymer molecular weight is less than the A block molecular weight; this criterion permits the A homopolymer to mix with and swell the A

block in what is known as a wet brush configuration. Provided the Flory χ parameter is sufficiently small, any homopolymer or solvent that is miscible with the A block can be used as an additive. Our work with nanostructured epoxies relies on miscibility between a polar block (e.g. PEO) and the epoxy resin, and immiscibility with a nonpolar block (e.g. PEP) to create this situation. Our preliminary discovery based on a symmetric PEP-PEO diblock, f_{PEO} = ½, revealed such phase behavior as illustrated in Figure 1a. These morphologies, except G, were preserved upon curing.

In order to manipulate the nanostructure at a given concentration we recently synthesized another set of PEP-PEO diblocks with asymmetric compositions. Figure 1b highlights the phase diagram obtained from one of these with f_{PEO} = 0.26. An inverted sequence of structures is evident, terminating in disordered vesicles at the lowest block copolymer concentrations. Again, all but the G phase survive curing. By shortening the relative length of the PEO block the interfacial curvature has been increased. As a consequence, a wide range of L phase replaces the G-C-S sequence in the symmetric case, while the spherical PEP micelles are converted to PEP bilayer sheets. This new vesicle morphology is highly desirable for enhancing toughness.
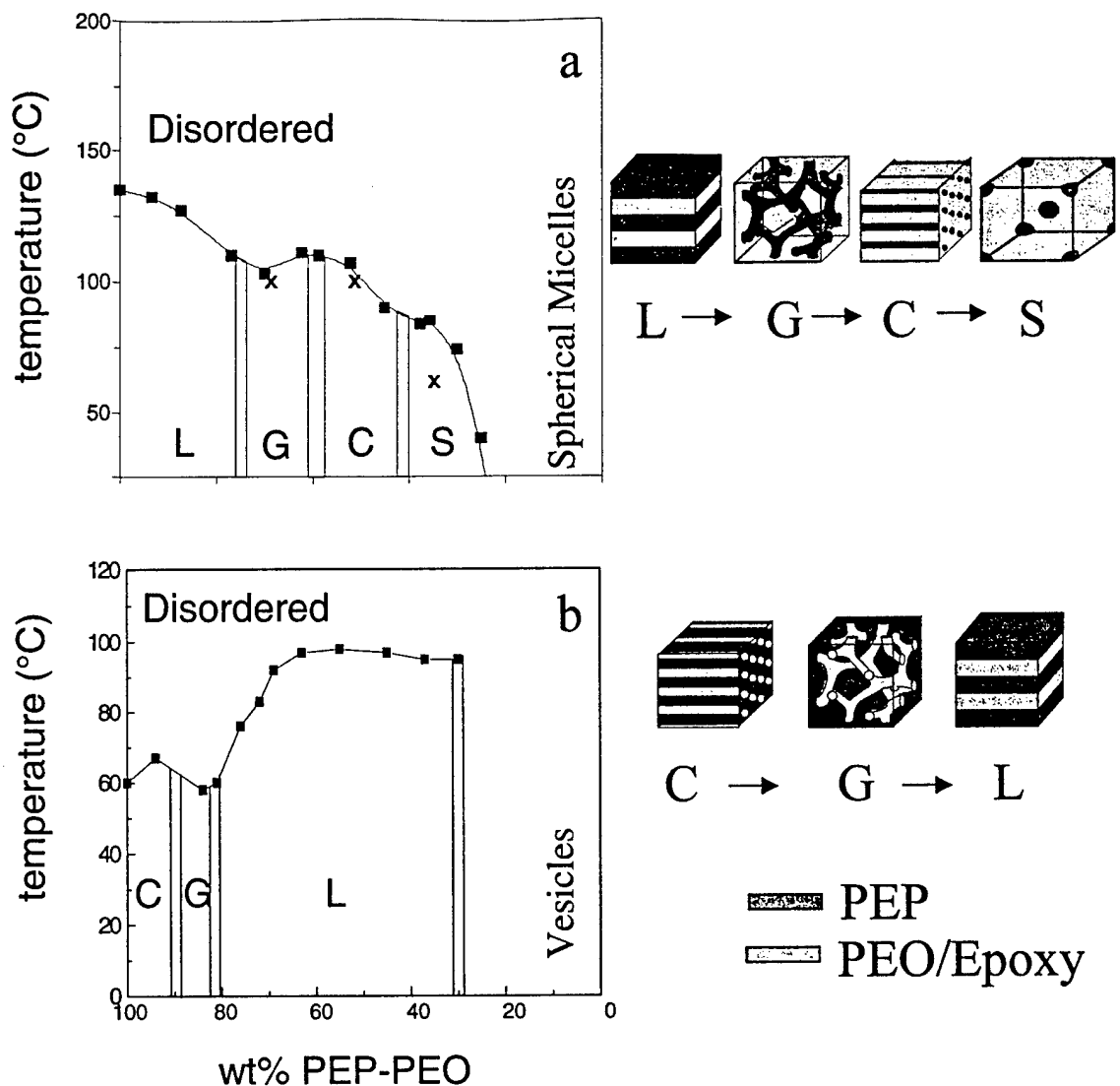
Figure 1. Phase diagrams for blends of PEO-PEP diblock copolymers with BPA348 epoxy. a.) Symmetric diblock (f_{PEO} = 0.51) produces a sequence of ordered phases that terminate in disordered spherical micelles. b.) Asymmetric diblock (f_{PEO} = 0.26) is characterized by a different sequence of ordered phases and vesicles at low block copolymer concentrations. All but the gyroid morphology survive curing with MDA.
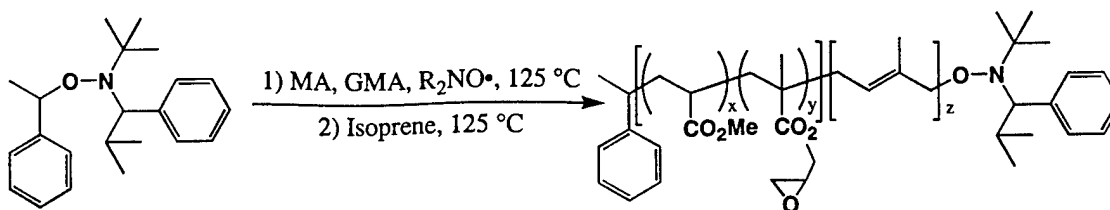
Reactive Block Copolymers

Based on success with the PEO-PEP block copolymers three new types of amphiphilic block copolymers were designed to provide control over interfacial bonding between the nanoscale inclusions and crosslinked epoxy matrix. The first of these was prepared through controlled oxidation of poly(diene) block copolymers, using dimethyldioxirane (DMD) generated *in-situ* from acetone and OXONE (potassium monopersulfate) during the reactions. This epoxidation reaction is highly selective towards 1,4 substituted poly(diene) repeat units. Our synthetic scheme can be summarized as follows:
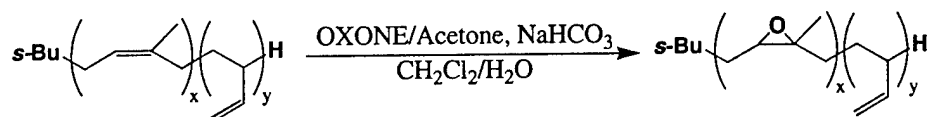
Scheme 1

The poly(butadiene)- poly(isoprene) block copolymers (PB-PI) were prepared using conventional anionic polymerization techniques, leading to 94 % 1,4 isoprene additions and 83% 1,2 butadiene additions. Upon reaction with DMD, approximately 90% of the epoxidation reaction occurs on the PI block, with the total extent of PI oxidation quantitatively determined by the amount of DMD present. We refer to these polymers as BIxn where n denotes the percent of epoxidized isoprene repeat units. This selective epoxidation leads to microphase separation of the neat diblock (M_n = 21,000 g/mol) when n > 42, and produces stable nanostructures in the BPA348/MDA epoxy resin when n > 80; when n ≤ 75 macrophase separation occurs during curing.

In order to incorporate less hindered, and hence more reactive, epoxy groups we designed a second type of partially epoxidized diblock copolymer using a nitroxide mediated living free radical approach.

Scheme 2

Here we have achieved both amphiphilicity and selective reactivity in diblock form by coupling non-polar PI to a random copolymer of methyl acrylate and glycidyl methacrylate. The product is refered to as MG-In, where n represents the volume fraction of poly(isoprene).

A third type of reactive diblock copolymer was synthesized using a metal mediated living free radical reaction.
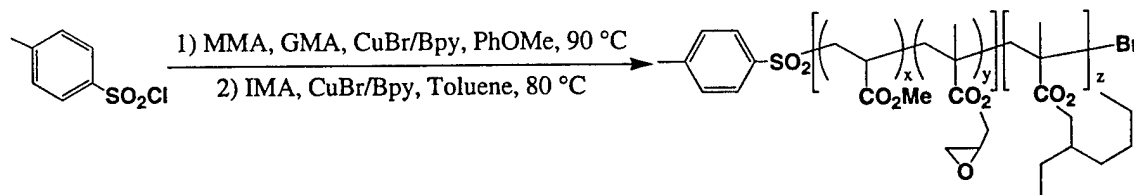
Scheme 3

The compound denoted MMG-IM combines the reactive glycidyl methacrylate-methyl acrylate random copolymer with poly(isooctyl methacrylate), a non-polar polymer with a bulky side group.

All three of these reactive block copolymers behave morphologically like PEO-PEP when blended with BPA348/MDA and cured, producing well-defined ordered and disordered structures. These results establish the generality of our approach.

Interfacial adhesion in the nanostructured epoxies is controlled by the rate of chemical "stitching" that occurs during curing. With PEO blocks there is no reaction and complete condensation of the epoxy monomers results in the expulsion of these blocks from the dense glassy network. BIxn can participate in network formation. However, the (mostly) backbone epoxy groups are significantly less reactive than the terminal BPA348 epoxy moieties, resulting in interfacial stitching following network formation.
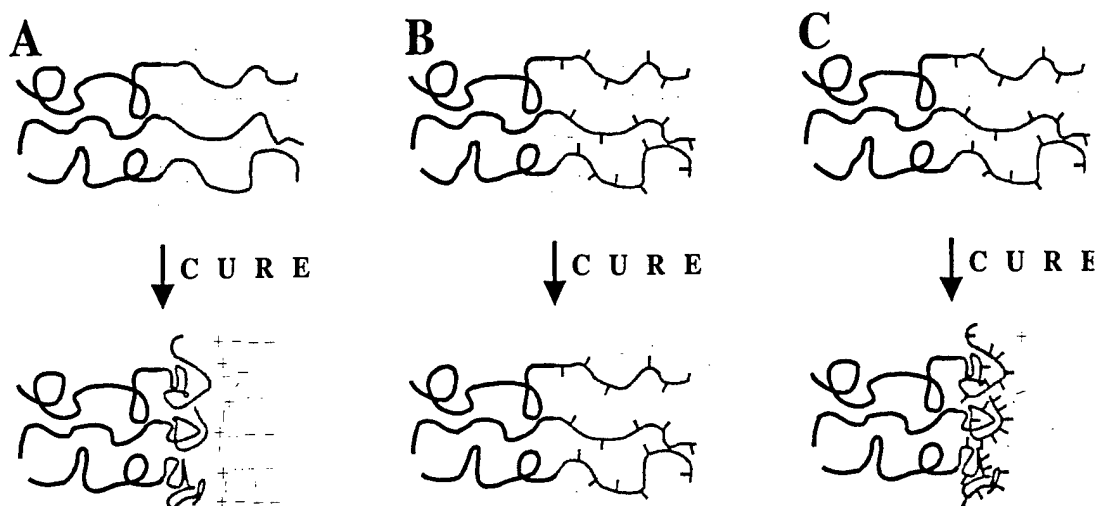
Figure 2. Illustration of the behavior of nonreactive (A) and reactive (B,C) block copolymer during curing in a thermosetting nanocomposite. A) Epoxy miscible block is ejected from matrix during crosslinking. B) Epoxy groups on block copolymer are isoreactive with resin and participate in crosslinking reaction. C) Epoxy groups on block copolymer react after network formation.

MG-In was designed to be isoreactive with BPA348, leading to uniform incorporation of the polymer chains into the epoxy network. These three cases are illustrated schematically in Figure 2. Differential scanning calorimetry (DSC) traces of epoxy blends containing BIx87 and MG-I50, shown in Figure 3, confirm that the former reacts long after the resin has cured while a single exotherm characterizes the reaction of the later. Representative TEM images illustrating example morphologies obtained from these new polymers are shown in Figure 4. All the ordered phases are accessible along with the vesicle and spherical micellar states. Curiously, to date we have not encountered worm-like micelles although this interesting and potentially useful morphology should be feasible.

Figure 3. DSC heating traces for the cure of 47 wt% BIx87 (gray) and 50% MG-I50 (black) blends with BPA348/MDA. The two exotherms evident in BIx87 indicate the sequential reaction of resin and block copolymer epoxy groups. With MG-I50 the block and matrix reactions occur simultaneously.
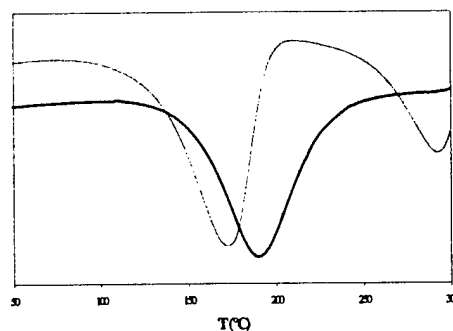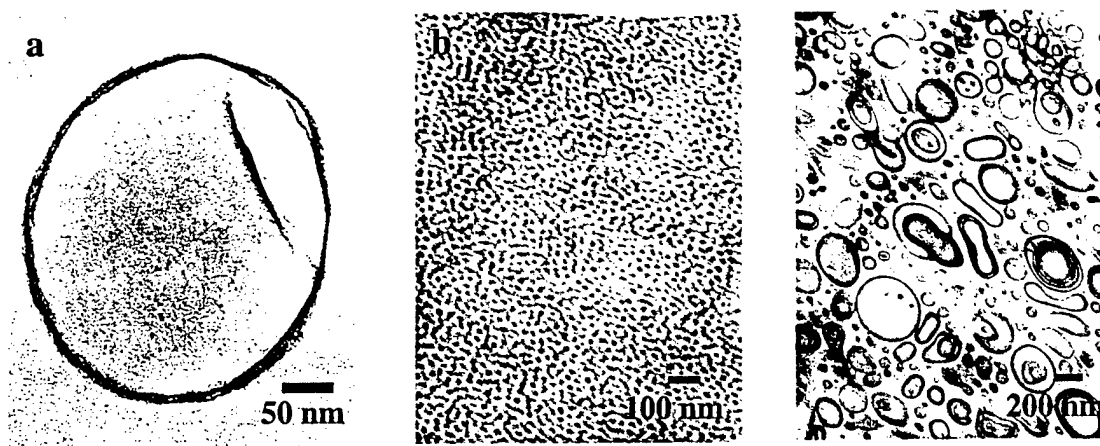
Figure 4. Representative TEM images showing various morphologies resulting from curing blends of block copolymers with BPA348/MDA. A) PEO-PEP vesicle at 2% loading; B) Disordered spheres of MG-170 at 20% loading; C) Vesicles of BIx87 at 20% loading. Contrast was obtained by staining with osmium tetraoxide.

Nanocomposite Toughness

The primary goal of this research is to explore new strategies for improving the mechanical properties of thermosetting plastics. Compact tension fracture tests have been employed to assess the effectiveness of various nanostructured inclusions as a function of block copolymer loading. The critical plain strain fracture toughness K_{1c} was determined using the ASTM D5045 test. Cracks were initiated in specimens machined from cured sheets of material using a razor blade followed by straining in tension on an Instron machine. Here we report the strain energy release rate, $G_c = K_{1c}^2 (1 - v^2)/E$, where v is Poisson's ratio, and E is the Young's modulus.

In all cases examined the addition of block copolymer led to an increase in G_c. Five percent by weight of spherical PEO-PEP micelles more than doubled the unmodified epoxy value (150 J/m^2). However, better improvement was realized when a vesicle morphology was used. Just two-and-a-half percent of the PEO-PEP vesicles led to a three-fold increase in G_c, accompanied by a dramatic change in the fracture surface. Figure 5 compares scanning electron microscopy images from the spherical and vesicle modified epoxy fracture surfaces. The former is nearly indistinguishable from that of the unmodified material, exhibiting relatively smooth fracture terraces. In contrast, the later contains micron size heterogeneities that reflect the vesicle structure. Both of these
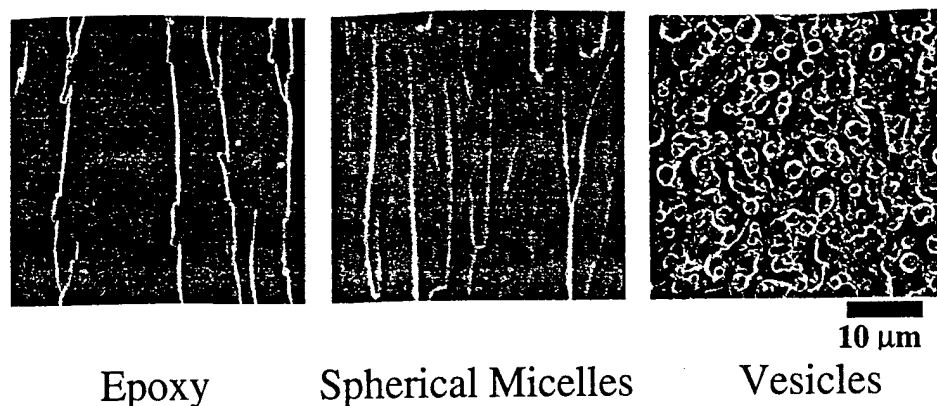
Epoxy   Spherical Micelles   Vesicles

Figure 5. SEM of fracture surfaces for unmodified epoxy (left), spherical micelle modified epoxy (center), and vesicle modified epoxy (right).

materials contain uncoupled interfaces between the particles and the matrix, i.e. case A in Figure 2.

Interfacial "stitching" (cases B and C in Figure 2) grossly affects particle/matrix adhesion in these epoxy nanocomposites as illustrated in Figure 6 for a fractured specimen containing vesicles of BIx87. Unlike the PEO-PEP vesicles, which cleanly separate from the epoxy matrix, all the "stitched" vesicles exhibit obvious interfacial adhesion manifested by fibrils that bridge the matrix-particle boundary.

We have found that the fracture energy can be correlated with particle diameter as shown in Figure 7. What makes this otherwise classical result significant is that two different operating curves appear to describe the data for PEO-PEP (case A), and BIxn and MG-In (cases B and C). Interfacial reaction leads to a much steeper enhancement in toughness with increasing particle size and the highest overall G_c values. Moreover, maximum fracture energy is obtained with just 2% by weight reactive block copolymer in contrast to 10% with the non-reactive material.

These failure properties are achieved with minimal reductions in other physical properties. DSC analysis revealed that the glass transition temperature of the cured resin is largely unaffected by the presence of the block copolymer up to about 10% loading. Dynamic mechanical spectroscopy tests show that nanospherical inclusions produce no perceptible change in the dynamic elastic modulus E' up to 5% loading. Vesicles have a greater impact on the modulus. Adding 5% block copolymer decreases E' by about 25%. This result reflects the fact that the vesicles enclose a sizable fraction of the crosslinked epoxy inside a thin rubbery shell, effectively creating holes that bear no load during a
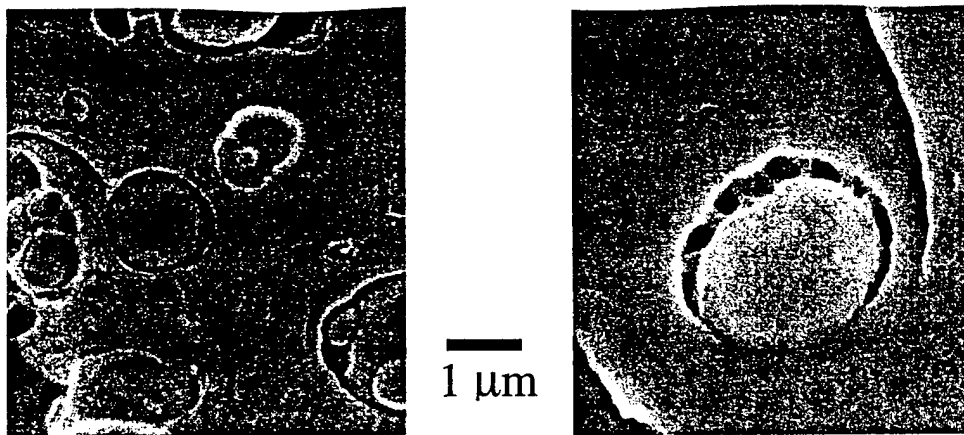
No Stitching   Stitching

Figure 6. Comparison of structure around vesicles prepared from non-reactive (left) and reactive (right) block copolymer. These samples were fractured prior to SEM imaging. Chemical stitching of the block copolymer corona to the crosslinked network is evident in the right image.
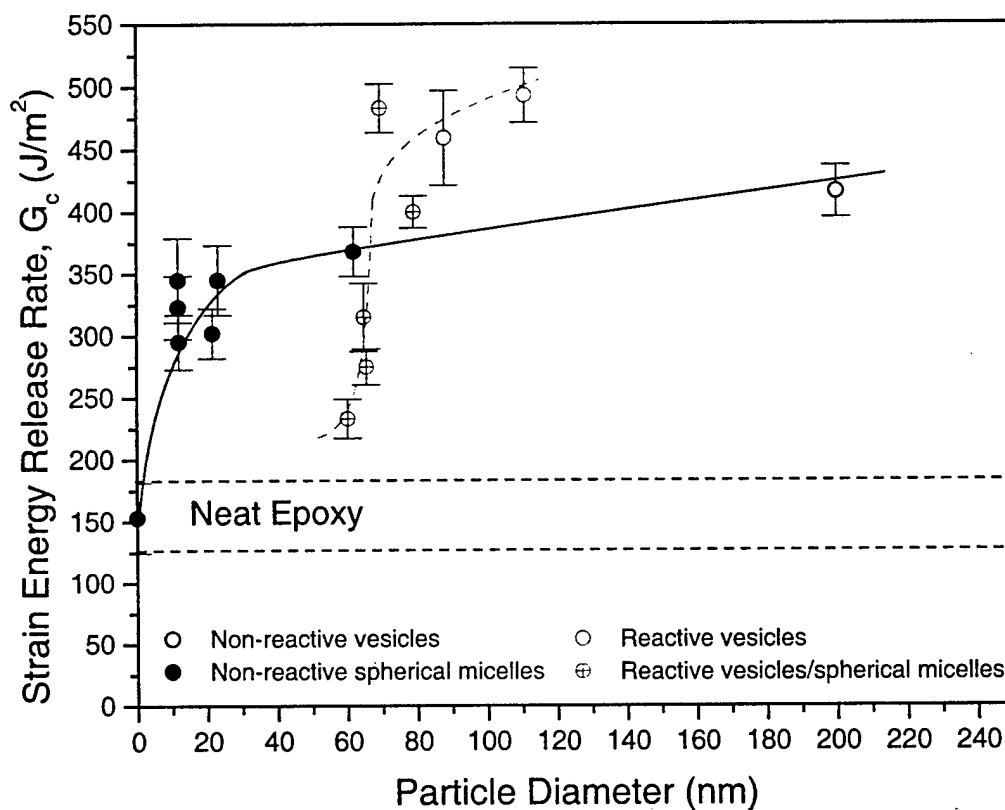

Figure 7. Correlation of fracture energy with particle diameter. Two operating curves are apparent, one for non-reactive (solid) and one for reactive (dashed) block copolymer. The highest value of G_c was obtained with just 2% block copolymer loading.

linear viscoelastic experiment. Similar effects are encountered with High Impact Polystyrene (HIPS) (perhaps the most successful engineered high impact plastic sold today) where a 30% reduction in the tensile modulus accompanies just 5% rubber loading. Ultimately, all relevant properties must be included in the overall assessment of the benefits associated with modifying a material.

Transition to Commercial Application

Two-part epoxies find numerous commercial applications, frequently involving fiberglass or carbon reinforcement. Electronic circuit boards are a prime example. These high tech components form the backbone of the microelectronics industry which is placing ever increasing demands on the limits of mechanical and dielectric properties, use temperature, ease of manufacturing, and of course low cost. Based on our success with the block copolymer modified BPA348/MDA, the Dow Chemical Company has engaged in a joint research and development project with the PI to assess the possibility of modifying their commercial circuit board formulations, mainly to improve the fracture resistance. This property plays a critical role in determining the smallest holes that can be created by drilling, a key manufacturing step in the production of circuit boards. These proprietary formulations are highly refined to incorporate the myriad requirements of the industry, including fire resistance, low water uptake, elevated glass transition temperature, a two stage thermal cure, and many more. In order to duplicate the vesicle morphology described above we must design suitable amphiphilic block copolymers that contain epoxy miscible and immiscible components. Preliminary results indicate that this is feasible. Duplication of the model morphologies in a commercial resin represents an important step in generalizing our results.

II.e   Bicontinuous Morphology

A remarkable feature of the epoxy nanostructure work is the absence of the gyroid morphology in the fully cured material. *In-situ* SAXS experiments have documented transformation of a PEO-PEP based G phase in the uncured state to lamellae upon crosslinking. Why does this happen? We speculate that it is a consequence of case A
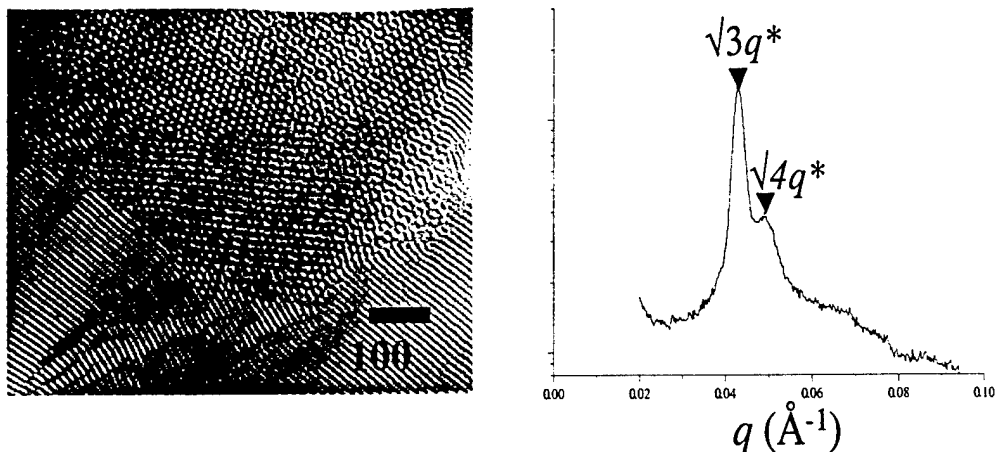
Figure 8. TEM (left) and SAXS (right) data identifying the gyroid phase in a cured BPA348/MDA – reactive diblock copolymer sample. The TEM image reveals coexistence of the G and L phases in this specimen while the two SAXS reflections are indicative of the G phase.

(Figure 2) behavior, i.e., the epoxy miscible block is squeezed out of the matrix during reaction thereby driving the spontaneous curvature away from that required for the G phase. Therefore, case B and C type reactive diblocks (Figure 2) should alleviate this restriction since block retraction is retarded through chemical "stitching". Preliminary experiments with an MG-I55 compound have met with partial success. Fully cured specimens that contain the G morphology have been prepared as evidenced by characteristic reflections in the SAXS patterns and TEM images (see Figure 8). However, in all instances encountered thus far we find coexistence between G and L. Thus, we have made progress in this aspect of the research and believe that within this final year of the current grant period a pure G modified nanocomposite will be realized.

Publications resulting from AFOSR support during the grant period:

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